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**ABSTRACT**

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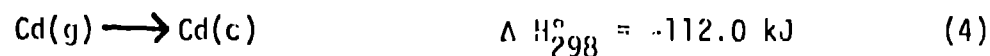
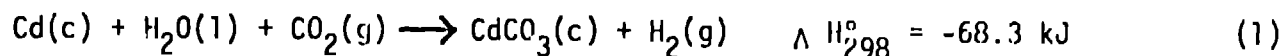
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## Studies on the LASL Cadmium-Cadmium Carbonate Cycle\*

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The LASL Cadmium-Cadmium Carbonate Cycle<sup>(1)</sup> was first presented at the I.E.A. Thermochemical Hydrogen Workshop in 1979.<sup>(2)</sup> The cycle can be summarized as follows:



The overall cycle has a figure of merit of 78% since the heat released by condensation of Cd, reaction (4), can be used for the thermal decomposition of  $\text{CdCO}_3$ , reaction (2).

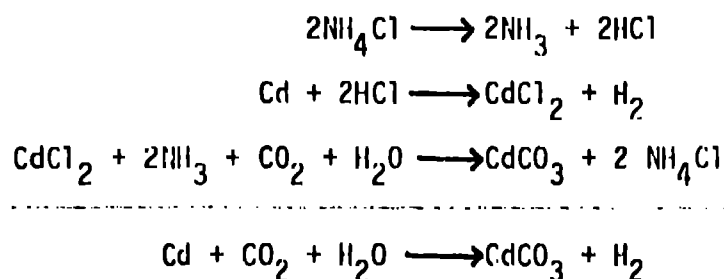
The thermal decomposition of CdO, reaction (3), is believed<sup>(3,4,5)</sup> to be a promising reaction for thermochemical cycles which can be powered by a solar heat source. A mass spectrometric investigation of the decomposition equilibrium of CdO(c) confirmed that CdO(c) vaporizes according to reaction (3) and that the literature thermodynamic data for reaction (3) is correct.<sup>(6)</sup> However CdO(g) was not observed in the equilibrium vapor of CdO(c) for temperatures up to 1150 K. This result gives a revised lower limit for the enthalpy of formation of CdO(g),  $\Delta H_{f,298}^\circ \geq 113.8 \text{ kJ mol}^{-1}$ . The Clausius-Clapeyron plot for Cd(g) and CdO(g) vapor pressures above CdO(c) is shown in Fig. 1. The upper limit for equilibrium pressure of CdO(g)

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is seen to be at least a factor of 15 lower than previously estimated at 1428 K. Therefore recombination between Cd(g) and O<sub>2</sub>(g) is less than previously believed. However, recombination between Cd(c) and O<sub>2</sub>(g) may still be significant.

The low temperature H<sub>2</sub> producing step, reaction (1), was extensively studied.<sup>(7)</sup> A surface reaction occurs with very slow H<sub>2</sub> evolution. The rate of H<sub>2</sub> evolution is dependent on the size of the Cd particles. When reaction conditions are held constant, (523 K, unstirred, 18 h, excess CO<sub>2</sub> and water) the H<sub>2</sub> evolved increases to 14% from 4% when the Cd particle size decreases to 9 μm from 20 μm.

Ammonium chloride was found to exhibit a marked catalytic effect<sup>(7)</sup> on reaction (1) as 72% of the available H<sub>2</sub> was formed in 1/2 h at 523 K using four-fold excess of NH<sub>4</sub>Cl, nine-fold excess of water, and three-fold excess of CO<sub>2</sub>. A proposed catalytic mechanism can be described by:



Although NH<sub>4</sub>Cl catalyses reaction (1) excess amounts of catalyst and partial formation of Cd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> are possible problems. Therefore a search was made for catalysts with fewer potential side reactions. Results of this search are given in Table 1. Palladium is seen to be the most effective catalyst of those investigated.

A kinetic investigation was carried out using Pd. The results are shown in Fig. 2 together with results from an uncatalysed experiment. Analysis of the data shown in Fig. 2 indicates that initial H<sub>2</sub> production follows an apparent first-order rate law and gives a rate-constant of 0.04 h<sup>-1</sup> for the

uncatalysed reaction and  $0.20 \text{ h}^{-1}$  for the catalysed reaction. For the catalysed reaction departure from first order kinetics occurs soon after the start of the reaction. For the uncatalyzed reaction, the kinetics exhibit a parabolic rate law,<sup>(8)</sup>  $x^2 = kt$ , where  $x$  is the thickness of the product  $\text{CdCO}_3$  layer (or amount of  $\text{H}_2$  production),  $t$  is the time and  $k$  is a constant. This indicates that the reaction is diffusion controlled due to the formation of  $\text{CdCO}_3$  around the Cd particles. The catalysed reaction did not appear to follow any simple rate law after departure from first-order kinetics, showing it is not diffusion controlled.

In an attempt to understand the mechanism of catalysis, a variety of soluble salts were tested for catalytic activity, and these are listed in Table 2.

$\text{PdCl}_2$  showed lower activity than Pd black but was investigated to show the catalytic behavior of a soluble Pd salt. However, when used in the presence of  $\text{CuCl}_2$ , the amount of  $\text{H}_2$  produced was similar to the amount formed using Pd black as a catalyst.  $\text{CuCl}_2$  was used as a catalyst as it is known to be a decarboxylation catalyst.<sup>(9)</sup>  $\text{CuCl}_2$  actually caused a reduction in  $\text{H}_2$  when used with Pd black, possibly due to the formation of  $\text{CdCl}_2$  which was found as a product in all cases when  $\text{CuCl}_2$  was used.

No clear catalytic mechanism was demonstrated by these studies. The catalytic activity exhibited by the catalysts investigated was still inferior to that exhibited by  $\text{NH}_4\text{Cl}$ . Nevertheless, the possibility of greater catalytic activity by an, as yet unidentified, agent cannot be ruled out.

The problem of drying  $\text{CdCO}_3$  (which is insoluble in water) prior to its thermal decomposition was briefly addressed. Figure 3 shows drying curves for  $\text{CdCO}_3$  at various temperatures.  $\text{CdCO}_3$  was slurred with water, filtered, and aspirated for 10 min, weighed and dried. The solid residue was found to be anhydrous  $\text{CdCO}_3$  as determined by its x-ray powder diffraction pattern.

Most of the water is removed by filtration prior to drying leaving behind 4 to 5 moles of water per mole of  $\text{CdCO}_3$ . Subsequent removal of this water is energetically expensive but compares favorably with the drying requirements of most other cycles currently under consideration.

In conclusion, we can summarize the results obtained:

1. A new lower limit for the heat of formation of  $\text{CdO(g)}$  has been estimated  $\Delta H_{f,298}^\circ > 113.8 \text{ kJ mol}^{-1}$ .
2. Hydrogen production is subject to catalysis. While Pd is an effective catalyst,  $\text{NH}_4\text{Cl}$  shows greater catalytic activity. Seventy-two percent of the total available  $\text{H}_2$  is formed in 1/2 h at 523 K using  $\text{NH}_4\text{Cl}$  as a catalyst.
3. Four to five moles of water must be removed from  $\text{CdCO}_3$  prior to its thermal decomposition.

#### REFERENCES

1. M. G. Bowman and C.F.V. Mason, Patent Disclosure, April 18 (1979).
2. C.F.V. Mason, J. D. Farr, and M. G. Bowman, Proc. I.E.A. Thermochemical  $\text{H}_2$  Workshop, LASL, LA-UR 79-2637, September(1979).
3. J. R. Pangborn, Proc. 1st World  $\text{H}_2$  Conference, Miami Beach, 1, 7A-59 (1976).
4. J. T. Porter, General Atomic Co., GA-A15700, February (1980).
5. C.F.V. Mason, M. G. Bowman, and R. G. Behrens, to be presented at 15th IECEC, August (1980).
6. R. G. Behrens and C.F.V. Mason, Submitted to J. of Less-Common Metals, April (1980).
7. C.F.V. Mason and M. G. Bowman, 3rd World  $\text{H}_2$  Energy Conference, Tokyo (1980).
8. K. J. Laidler, Chemical Kinetics, McGraw-Hill Book Co. (1965).
9. J. E. Prue, J. Chem Soc., 2331(1952).

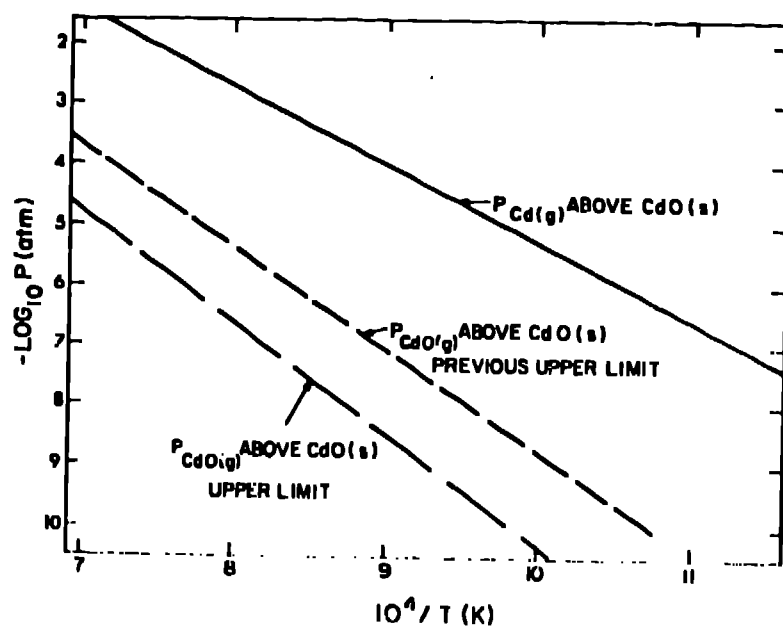


Fig. 1. Clausius - Clapeyron plot for Cd(g) and CdO(g) vapor pressures above CdO(c).

Table 1. Effect of various catalysts on  $\text{H}_2$  production. 9gm Cd, 3h, 448 K,  $\text{CO}_2$  8.21x10<sup>-2</sup> mol,  $\text{H}_2\text{O}$  22.2x10<sup>-2</sup>.

Cd x 10 <sup>-3</sup> m	Catayst	Mole Cat/Mole Cd	H <sub>2</sub> mol	Mole H <sub>2</sub> /Mole Cd
7.59	Pt, 325 mesh	0.15	2.3 x 10 <sup>-5</sup>	0
7.66	Pd black	0.11	1.45 x 10 <sup>-3</sup>	0.19
7.53	Ru	0.14	2.95 x 10 <sup>-4</sup>	0.04
7.85	Rh powder	0.10	2.3 x 10 <sup>-5</sup>	0
7.61	Zr powder	0.21	1.4 x 10 <sup>-4</sup>	0.01
7.73	- - - -	- - -	2.3 x 10 <sup>-5</sup>	0

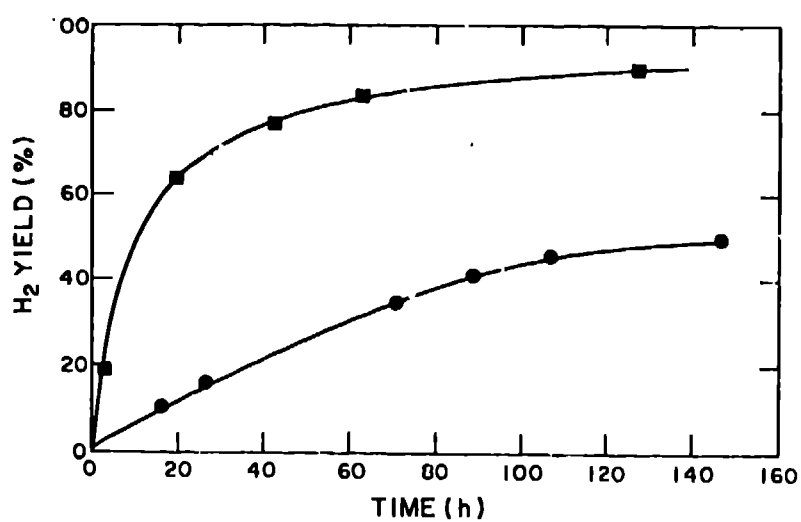


Fig. 2. H<sub>2</sub> produced as a function of time. (9  $\mu$ m Cd  $6.6 \times 10^{-3}$  mole, H<sub>2</sub>O  $22.2 \times 10^{-2}$  mole, CO<sub>2</sub>  $8.21 \times 10^{-2}$  mole, 448 K).

● uncatylased  
■ Pd black catalysed

Table 2. Effect of various catalysts on H<sub>2</sub> production.

9  $\mu$ m Cd, 18 h, 448 K, CO<sub>2</sub> =  $8.21 \times 10^{-2}$  mol. H<sub>2</sub> =  $22.2 \times 10^{-2}$  mol.  
mol. cat./ mol. Cd = 0.1

Cd 10 <sup>-3</sup> mol.	catalyst	H <sub>2</sub> 10 <sup>-3</sup> mol.	mol. H <sub>2</sub> /mol. Cd
8.23	Pd black	4.81	0.58
8.07	PdCl <sub>2</sub>	2.27	0.28
8.42	PdCl <sub>2</sub> , CuCl <sub>2</sub>	4.65	0.55
7.66	CuCl <sub>2</sub>	1.25	0.16
8.40	Pd black, CuCl <sub>2</sub>	3.75	0.45
6.55	" " " " " "	0.68	0.10

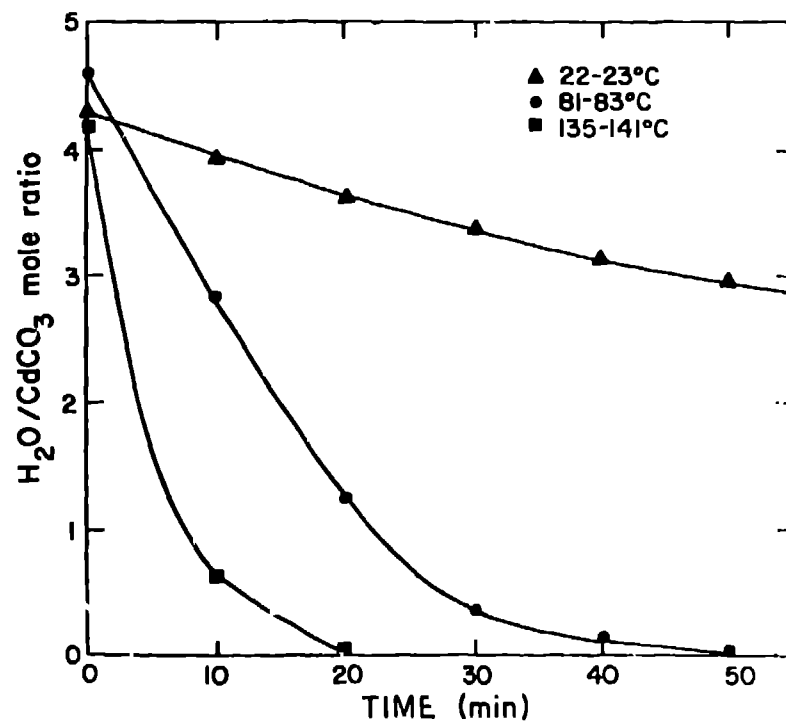


Fig. 3. Drying curves for cadmium carbonate as a function of temperature.